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Reactions of Triply-bonded Dimetal Compounds.
Reversible Addition of Carbon Monoxide to a Hexakis(alkoxy)
dimolybdenum Compound. A Molecule with a
Carbonyl-bridged Metal-to-Metal Double Bond.

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Princeton, New Jersey 08540

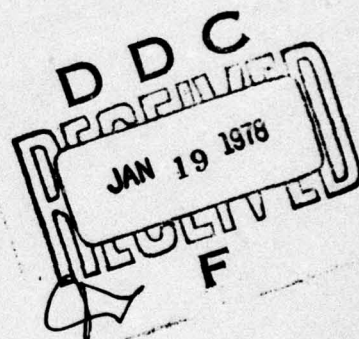
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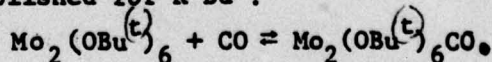
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The dinuclear alkoxides, $\text{Mo}_2(\text{OR})_6$, which contain metal-to-metal triple bonds, react with carbon monoxide at room temperature and 1 Atmos. A reversible reaction has been established for $\text{R}=\text{Bu}^t$:



The compound $\text{Mo}_2(\text{OBu}^t)_6\text{CO}$ has been structurally characterized and shown to contain a carbonyl-bridged metal-to-metal double bond. The Mo-to-Mo distance

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is 2.489(1)A. In the presence of an excess of CO, Mo(CO)₆ is ultimately formed along with other as yet, uncharacterized molybdenum containing compounds.

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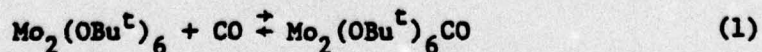
Reactions of Triply-bonded Dimetal Compounds. Reversible Addition of Carbon Monoxide to a Hexakis(alkoxy)dimolybdenum Compound. A Molecule with a Carbonyl-bridged Metal-to-Metal Double Bond.

Sir:

We report here our initial observations on a series of most remarkable reactions involving carbon monoxide and $\text{Mo}_2(\text{OR})_6$ compounds, which contain unbridged metal-to-metal triple bonds.¹

Alkane solutions of $\text{Mo}_2(\text{OR})_6$ compounds where $\text{R} = \text{Me}_3\text{C}$, Me_2CH and Me_3CCH_2 , rapidly absorb carbon monoxide at room temperature to give dark solutions.² Upon exposure to two equivalents of CO, crystalline compounds have been obtained merely by cooling the alkane solutions to ca. -10°C . Black crystalline compounds of empirical formula $\text{Mo}(\text{OR})_3\text{CO}$ have been obtained for $\text{R} = \text{Me}_2\text{CH}$ and Me_3CCH_2 and a preliminary X-ray investigation has shown that the isopropoxide is tetranuclear, $\text{Mo}_4(\text{OPr}^i)_{12}(\text{CO})_4$. The IR spectrum of the latter compound shows four well-resolved and sharp bands of approximately equal intensity assignable to coordinated carbonyl ligands: 1957, 1882, 1837 and 1819 cm^{-1} . When $\text{R} = \text{Me}_3\text{C}$, a dark purple crystalline compound, $\text{Mo}_2(\text{OBu}^t)_6\text{CO}$, I, was obtained which showed only one IR band, at 1670 cm^{-1} , assignable to a carbonyl group.

All the new carbonyl compounds are thermally labile. I readily loses CO on heating in vacuo and $\text{Mo}_2(\text{OBu}^t)_6$ is recovered. Carbon monoxide is also lost in solution under a nitrogen purge or under vacuum. This establishes the reversibility of reaction 1 below.



The black crystalline compounds, $\text{Mo}_4(\text{OR})_{12}(\text{CO})_4$, where $\text{R} = \text{Me}_2\text{CH}$ and Me_3CCH_2 , yield $\text{Mo}(\text{CO})_6$ at 50°C , 10^{-2} Torr and $\text{Mo}_2(\text{OR})_8$ compounds at $80-100^\circ\text{C}$, 10^{-2} Torr. Other non-volatile products are as yet uncharacterized in these thermal decomposition reactions.

Upon exposure to an excess of CO (1 Atmos) $\text{Mo}_2(\text{OR})_6$ compounds react further. For example, after exposing a hexane solution of $\text{Mo}_2(\text{O}^t\text{Bu})_6$ to an excess of CO (1 atmos) for 12 hr the solvent was stripped, leaving a black powdery residue which showed the following IR bands assignable to carbonyl groups: 2022m, 1985vs, four overlapping bands at ca. 1930, all strong, 1830w, 1690vw, 1670w and 1630w cm^{-1} . The band at 1985 cm^{-1} is assignable to $\text{Mo}(\text{CO})_6$ and even at room temperature, 1 atmos, this compound slowly sublimes out of the black residue. Thus it appears that formation of I represents merely the first step in a chain of reactions which leads to $\text{Mo}(\text{CO})_6$ amongst other as yet uncharacterized products. We proceeded directly toward a full structural characterization of the novel carbonyl compound, I.

Crystals of I consist of discrete dinuclear molecules with the structure shown in Fig. 1. Here we omit, for the sake of clarity, the $(\text{CH}_3)_3\text{C}$ groups. Each molecule possesses a crystallographically⁴ imposed mirror plane containing O1, C1, O2 and O3 and bisecting the Mo-Mo bond. The virtual symmetry of the molecule is C_{2v} . The coordination polyhedron about each metal atom is a distorted square pyramid with the Mo to carbonyl carbon bond at the apex.

We believe the Mo-Mo bond has a formal bond order of 2. The molecule is diamagnetic and the electron counting for each molybdenum atom may be conducted as follows: the neutral Mo atom has 6 electrons, each terminal RO group contributes 1 as does the bridging CO group, and the pair of bridging RO groups contribute 3 electrons to each metal atom. Thus, before metal-metal

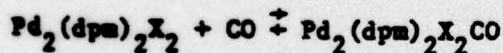
bond formation is considered, each metal atom has 12 electrons. To account readily for diamagnetism, an Mo-Mo bond of even order should be present. With a distance of 2.489(1)Å, the only reasonable conclusion is a bond order of 2.

Metal to metal bonds of orders 1, 3 and 4 are, of course, very numerous and well-known, but not many double bonds have been observed to date. For molybdenum there have not previously been any unambiguous cases⁵ except for that in Mo₂(OPr¹)₈,⁶ where the Mo-Mo distance, 2.523(1)Å, is very similar to the one found here. It is noteworthy that in the isopropoxide also the metal atoms have formal 14-electron configurations, but the coordination polyhedron is a trigonal bipyramid.

In conclusion we emphasize the following:

1) This work provides the first synthesis and structural characterization of a compound in which a carbonyl ligand bridges a metal-to-metal double bond, as well as only the second unambiguous example of an Mo = Mo bond.

2) To our knowledge the reversible reaction 1 has but one analogy, namely, the recently reported reversible CO insertion into a Pd-Pd single bond.⁷



where X = Cl, Br and dpm = Ph₂PCH₂PPh₂.

3) The formation of Mo(CO)₆ under the extremely mild conditions reported here is quite remarkable. Indeed, the reaction between Mo₂(OR)₆ compounds and CO may prove synthetically useful for the synthesis of labelled compounds Mo(*CO)₆.

Supplementary Material. A Table (1 page) of atomic positional and thermal parameters. Ordering information is given on any current masthead page.

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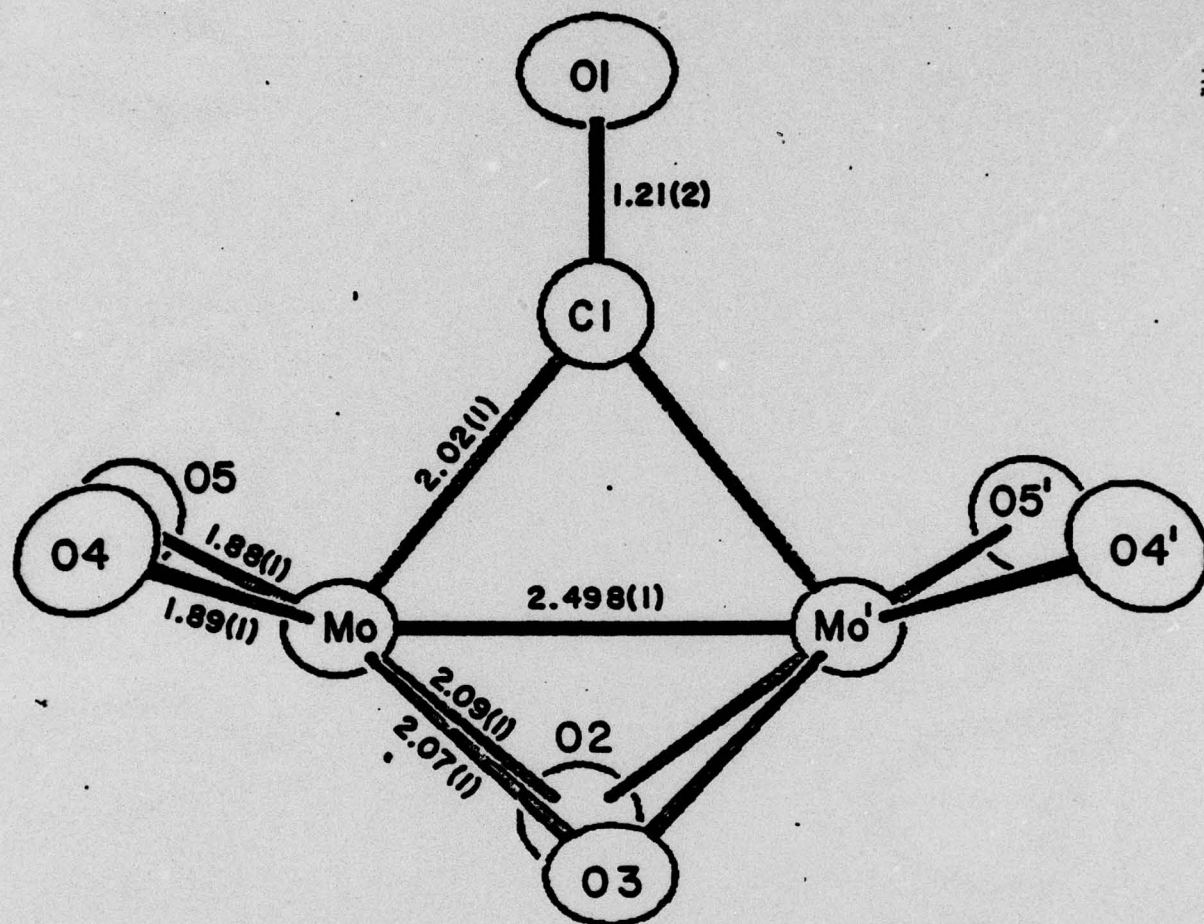
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2. Additions were made using standard vacuum line techniques.
3. For $\text{Mo}(\text{OCHMe}_2)_3\text{CO}$, Anal calcd (found): C, 39.88(39.88); H, 7.03(7.06).
4. Crystal data for $\text{Mo}_2(\text{O}-t\text{-Bu})_6(\text{CO})$: $a = 17.827(3)$, $b = 9.335(2)$, $c = 19.447(4)\text{\AA}$, $\alpha = \beta = \gamma = 90.00^\circ$, $V = 3236(1)\text{\AA}^3$, $Z = 4$. Space group $C_{2h}1$ (No. 36). Unique data (1532 reflections) having $0.0^\circ < 2\theta(\text{MoK}\alpha) < 50.0^\circ$ were collected at 22°C using $\text{MoK}\alpha$ radiation ($\alpha = 0.710730\text{\AA}$) and the 1237 reflections having $I > 3\sigma(I)$ were retained as observed. The structure was solved using standard heavy atom methods and refined to convergence utilizing anisotropic thermal parameters for molybdenum and oxygen atoms and isotropic thermal parameters for the carbon atoms. Hydrogen atoms were not located. Final residuals are $R = 0.067$ and $R_w = 0.085$; the esd of an observation of unit weight was 1.958.
5. F. A. Cotton, J. Less-Common Metals, **54**, 3 (1977).
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8. Alfred P. Sloan Fellow, 1976-78.

Figure 1. A view of the coordination geometry of I, $\text{Mo}_2(\text{OBu}^t)_6(\text{CO})$, showing the main internuclear distances. Each atom is represented by its ellipsoid of thermal vibration, scaled to enclose 40% of the electron density. The tertiary butyl groups are omitted for clarity.



POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS.

ATOM	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
ND	-0.07006(5)	-0.26838(8)	-0.2500(8)	0.00236(3)	0.00649(8)	0.00163(2)	-0.00009(9)	-0.0002(1)	-0.0001(3)
O1	0.0000(8)	-0.557(1)	-0.2891(8)	0.0044(6)	0.007(1)	0.0034(4)	0.000(8)	0.0000(8)	0.0018(15)
O2	0.0000(8)	-0.187(1)	-0.1731(6)	0.0030(5)	0.010(2)	0.0014(3)	0.000(8)	0.0000(8)	-0.0012(12)
O3	0.0000(8)	-0.121(1)	-0.2971(7)	0.0028(4)	0.006(1)	0.0021(3)	0.000(8)	0.0000(8)	0.0011(12)
O4	-0.1357(6)	-0.279(1)	-0.3260(5)	0.0034(3)	0.010(1)	0.0017(2)	-0.002(1)	-0.0017(5)	0.0009(9)
O5	-0.1337(5)	-0.359(1)	-0.1867(5)	0.0027(3)	0.011(1)	0.0023(3)	-0.001(1)	0.0012(5)	-0.0003(10)
C1	0.0000(8)	-0.432(2)	-0.2730(9)	2.8(3)					
C2	0.0000(8)	-0.149(2)	-0.1040(12)	4.1(4)					
C3	0.0000(8)	-0.279(3)	-0.0586(16)	6.2(6)					
C4	-0.0693(10)	-0.058(3)	-0.0875(12)	6.8(5)					
C5	0.0000(8)	0.034(2)	-0.3047(11)	3.9(4)					
C6	0.0000(8)	0.066(4)	-0.3785(28)	9.1(10)					
C7	0.0604(11)	0.094(2)	-0.2720(10)	6.3(5)					
C8	-0.1554(10)	-0.323(2)	-0.3940(9)	5.0(3)					
C9	-0.1227(13)	-0.467(3)	-0.4065(12)	7.8(5)					
C10	-0.2431(13)	-0.338(3)	-0.3919(13)	7.5(5)					
C11	-0.1360(21)	-0.202(4)	-0.4422(19)	10.8(8)					
C12	-0.1689(8)	-0.483(2)	-0.1577(8)	4.1(3)					
C13	-0.2171(10)	-0.434(2)	-0.0991(11)	5.9(4)					
C14	-0.2193(13)	-0.541(3)	-0.2175(12)	8.0(6)					
C15	-0.1129(11)	-0.593(2)	-0.1396(9)	5.5(4)					

THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS:

$$\text{EXP}[-(B(1,1) * H * H + B(2,2) * K * K + B(3,3) * L * L + B(1,2) * H * K + B(1,3) * H * L + B(2,3) * K * L)]$$

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